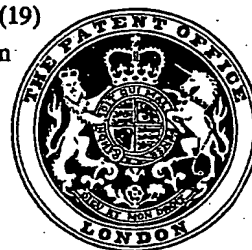


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 (72) Inventor: Hans-Jurgen Pettelkau



(54) CONCENTRATED POLYCHLOROPRENE LATICES WITH REACTIVE GROUPS

(71) We BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 This invention relates to a process for the production of concentrated polychloroprene latices containing reactive groups by copolymerising chloroprene with an olefinically unsaturated carboxylic acid in aqueous emulsion at pH-values ≤ 7 in the presence of known emulsifiers and radical initiators. 5

10 Films of polychloroprene latices without any reactive groups have to be crosslinked with zinc oxide and magnesium oxide in the presence of vulcanisation aids and at elevated temperature in order to obtain the valuable service properties required. 10

By contrast, films of polychloroprene latices containing reactive groups can be crosslinked with zinc oxide and magnesium oxide at temperatures as low as room temperature along the lines of a vulcanisation process.

15 Polychloroprene latices containing reactive groups are known. Their production is described in German Auslegeschrift No. 1, 103, 569. In this process, however, a further monomer, for example butadiene, has to be used in addition to chloroprene and an ethylenically unsaturated carboxylic acid for the copolymerisation reaction. The use of latices such as these, for example for the production of films and coatings, has also been described (cf. H. Esser, Baypren-Latices und ihre industriellen Anwendungen; Gummi, Asbest, Kunststoffe, 20 1973, Nos. 5-7, pages 394-398, 494-503, 574-582). 20

The solids content required for processing latices of this kind amounts to about 50% by weight (cf. Bayer-Handbuch für die Gummi-Industrie, 1971, pages 209 *et seq.*, Publishers: Bayer AG, Leverkusen).

25 It is only possible to obtain latices with a solids content of at most 44% by weight with the process described in German Auslegeschrift No. 1, 103, 569. Accordingly, the latices have to be concentrated by known methods, for example the methods described in German Patent Specification No. 727, 534, British Patent Specification No. 382, 235 or in US Patent Specification No. 2, 405, 724. 25

30 Accordingly, the process for producing the concentrated latex is a two-stage process. 30

Concentration of the latex by evaporation *in vacuo* is difficult to control because the latex foams to a very considerable extent. In the "creaming" method, an emulsifier and polymer-containing "serum" with a solids content of up to 4% by weight is obtained, its safe elimination being difficult and expensive. For these reasons, there was a need to find a one-stage process by which it would be possible to produce polychloroprene latices containing reactive groups with solids contents of more than 50% by weight and having the same favourable service properties. 35

40 German Auslegeschrift No. 1, 103, 569 describes the copolymerisation of chloroprene with an olefinically unsaturated carboxylic acid as an extremely violent reaction which is accompanied by a considerable heat effect and which is therefore difficult to control. It has now been found that this copolymerisation reaction can be carried out under control and without any problem whilst, at the same time, reducing the quantity of water used and increasing the monomer conversion by using a carefully co-ordinated recipe of the emulsion components. It is possible in this way to obtain reproducible products with equally good service properties. 45

The present invention relates to a process for the production of concentrated polychloroprene latices containing reactive groups by copolymerising chloroprene with an olefinically unsaturated monocarboxylic or dicarboxylic acid, distinguished by the fact that from 75 to 95 parts by weight of water are used per 100 parts by weight of the monomer mixture and from 3 to 6 parts by weight of at least one ionic emulsifier active in the acid and neutral pH-range, optionally together with from 0.5 to 6 parts by weight of at least one non-ionic emulsifier active in the acid and neutral pH range, optionally together with from 0.5 to 6 parts by weight of at least one non-ionic emulsifier and from 0.2 to parts by weight of one or more other surface active substances, based in each case on 100 parts by weight of the total monomer mixture, and polymerisation is carried out at a pH value of ≤ 7 and at a temperature of from 30 to 70°C up to a monomer conversion of at least 90%.

Examples of olefinic carboxylic acids copolymerisable with chloroprene are acrylic acid, methacrylic acid, itaconic acid, maleic acid and vinyl acetic acid preferably used in quantities of from 0.5 to 10 parts by weight per 100 parts of monomer, the expression "monomer" relating to the sum total of parts by weight of chloroprene and the olefinically unsaturated carboxylic acid.

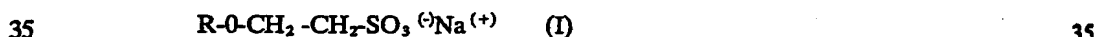
It is preferred to use olefinically unsaturated mono carboxylic acids and particularly preferred to use acrylic acid and methacrylic acid.

The presence of a third copolymerisable monomer is not necessary for carrying out the process according to the invention. However, additional monomers may, of course, be used for copolymerisation if desired.

Polymerisation is carried out in known manner in the form of an emulsion polymerisation reaction either continuously or in batches.

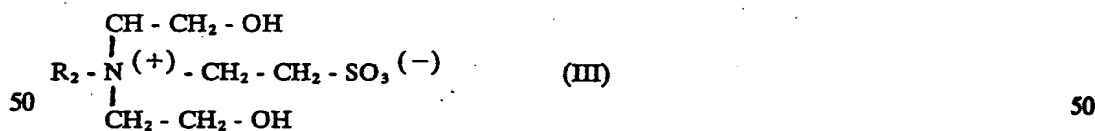
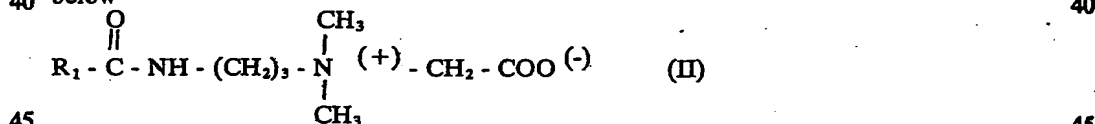
The quantities of emulsifier used are governed by the stability and viscosity of the emulsion during the polymerisation reaction, by the colloidal stability of the latex produced and by the quantity of any coagulate formed during polymerisation.

Examples of ionic emulsifiers are the alkali metal salts of derivatives of sulphuric acid and phosphoric acid, for example their sodium or potassium salts. The following are mentioned by way of example: alkyl sulphonates with from 8 to 20 carbon atoms in the alkyl radical; nucleus-alkylated benzene sulphonates with from 1 to 20 carbon atoms in the alkyl radical; sulphosuccinic acid esters, amides and amide esters with from 5 to 20 carbon atoms in the alcohol component; isothionates corresponding to the formula (I):



in which R = C₈-C₂₀-alkyl; and alkali metal salts of alkyl sulphuric acids or monoalkyl or dialkyl phosphoric acids with from 8 to 20 carbon atoms in the alcohol component.

It is also possible, for example, to use betaines corresponding to formulae (II) and (III) below



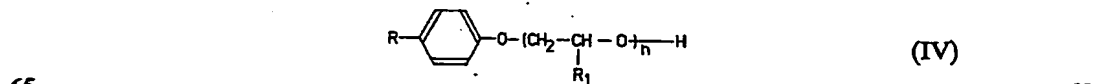
where R₁ and R₂ = C₈-C₂₀-alkyl.

The quantities of ionic emulsifier required vary from 3 to 6 parts by weight per 100 parts of monomer, according to the effectiveness of the compound used, the range from 3 to 4 parts by weight being preferred.

The effect of the ionic primary emulsifiers may be improved *inter alia* by adding from 0.5 to 6 parts by weight of a non-ionic emulsifier.

In particular, the following classes of compounds are mentioned by way of example:

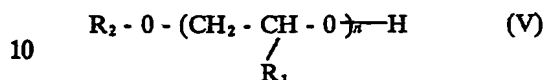
a) Ethylene oxide or propylene oxide adducts of substituted phenols and alcohols corresponding to formulae (IV) and (V) below:



in which

R represents a branched and/or unbranched C₁-C₂₀-alkyl radical, a phenyl radical and/or a phenyl radical alkyl-substituted once of several times with C₁-C₂₀-carbon atoms in the alkyl chain,

R₁ represents a hydrogen atom or a methyl group, and
n is a number from 1 to 30;

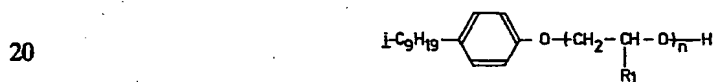


in which

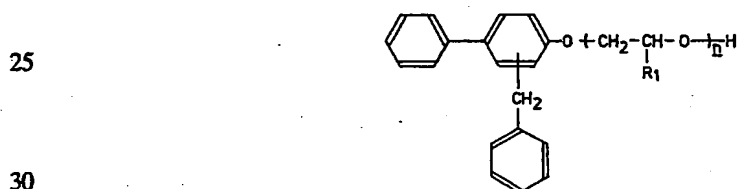
R₂ represents a branched and/or unbranched, saturated and/or unsaturated aliphatic hydrocarbon radical with from 10 to 30 carbon atoms,

15 and
R₁ and n are as defined above.

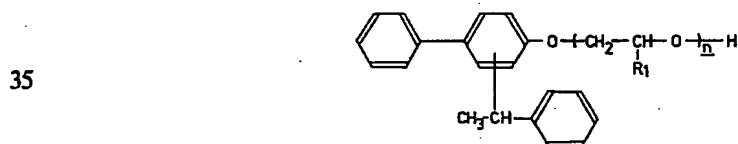
The following compounds are mentioned in particular:



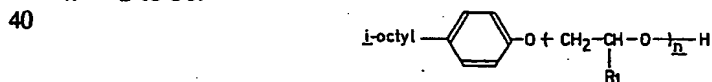
n = 2 to 30.



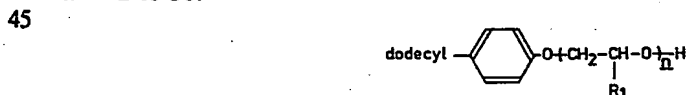
30 n = 2 to 30.



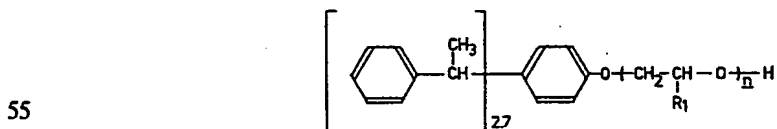
n = 2 to 30.



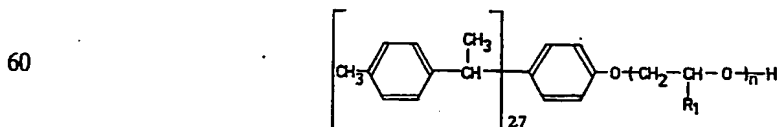
n = 2 to 30.



50 n = 2 to 30.



n = 2 to 30.



n = 2 to 30.

65

- b) Alkylene oxide or propylen oxide reaction products with cetyl alcohol, lauryl alcohol, stearyl alcohol, decyl alcohol, oleyl alcohol, the number of alkylene oxide units amounting in each case to between 2 and 30;
- 5 c) Fatty acid polyoxalkylates corresponding to the formula: 5

$$R-CO-(\text{---} O - CH_2 - CH_2 \text{---})_m - OH,$$
in which the radical R represents $C_n H_{2n} + 1$, $C_{n1} H_{2n1} - 1$, or $C_{n2} H_{2n2} - 3$,
10 n is a number from 6 to 25, n_1 and n_2 are numbers from 9 to 23 and m is a number from 1 to 30.
The following are mentioned as examples of fatty acids: lauric acid, oleic acid and stearic acid.
- 15 d) Fatty acid amide polyoxalkylates corresponding to the formula (VI): 15

$$R - CONH-(\text{---} CH_2 - CH - O \text{---})_m - H \quad (VI)$$

\downarrow
 R_1

in which
20 R represents a radical R as already defined under c), and m is a number from 2 to 30.
The following are mentioned as examples of acid components: stearic acid, palmitic acid and oleic acid.
- In all the above formulae, the radical R_1 represents hydrogen or methyl.
- 25 In addition, the condensation product of naphthalene sulphonic acid and formaldehyde, dialkyl naphthalene sulphonates and the condensation product of oxydiphenyl sulphonic acid and formaldehyde are examples of surfactants which may be used as further surface-active substances in quantities of from 0.2 to 2.0 parts by weight per 100 parts of monomer, the range from 0.4 to 1.0 part by weight being preferred. The emulsifiers and surface active
30 substances may be used either individually or in admixture, the quantities being governed by the limits specified.
- The structure and properties of the copolymers may be varied within wide limits by the addition of known modifying compounds such as, for example, mercaptans, xanthogen disulphides, etc.
- 35 From 75 to 95 parts by weight of water per 100 parts by weight of total monomer are used for producing the high solids latices.
- The polymerisation initiators used are the known compounds which form free radicals, such as for example hydrogen peroxide, alkali metal peroxydisulphates, water-soluble salts of persulphuric acid, organic peroxides (for example p-menthane hydroperoxide) and, with
40 particular advantage, formamidine sulphinic acid in accordance with German Auslegeschrift No. 1, 097, 689.
- The polymerisation reaction is carried out at temperatures in the range of from 30 to 70°C, although it is preferably carried out at temperatures in the range of from 40 to 65°C.
- The emulsion has a pH value of up to 7, the pH-range of from 3 to 6.5 being preferred.
- 45 Fluctuations in pH during polymerisation may be limited by using a buffer, for example a phosphate buffer.
- In every case, the monomer is reacted to a conversion of at least 90%, a conversion of from 97 to 99.8% being preferred.
- Unreacted organic compounds may be removed from the latex by steam distillation, for
50 example at 50°C under an absolute pressure of 20 Torr.
- The invention is illustrated by but by no means limited to the following Examples. All percentages are by weight unless otherwise indicated.
- The solids content of the latices is determined by removing water and other volatile components from a preweighed sample at 120°C in a vacuum drying cabinet. The weight of
55 the dry sample is determined and the solids content is expressed in %, based on the weight of the original sample.
- EXAMPLE 1**
- An aqueous phase (W) and a monomer phase (M) were emulsified:
- Aqueous phase (W):*
- | | | |
|--|----------------------|----|
| 60 Desalted water | 85.0 parts by weight | 60 |
| Paraffin Sulphonate | 3.0 parts by weight | |
| Adduct of 1 mole of stearyl alcohol and 20 moles of ethylene oxide | 1.0 part by weight | 65 |

	Adduct of 1 mole of nonyl phenol and 20 moles of ethylene oxide	0.3 part by weight		
	Potassium peroxydisulphate	0.001 part by weight		
5	<i>Monomer phase (M):</i>		5	
	Chloroprene (stabilised with 100 ppm of phenothiazine)	98.0 parts by weight		
10	Methacrylic acid (stabilized with 50 ppm of hydroquinone methyl ether)	2.0 parts by weight	10	
	<i>n</i> -dodecyl mercaptan	0.3 part by weight		
15	The emulsion was heated with stirring under a nitrogen atmosphere. The reaction began at 40°C and necessitated cooling. The polymerisation temperature fluctuated between 40 and 44°C and the polymer content increased uniformly. The polymerisation reaction was over after 4 hours (concentration of the latex after evaporation of H ₂ O and volatile compounds: 53.7%, pH 5.8). No coagulate was formed during polymerisation. The conversion amounted to approximately 99%. After standing for 2 months, the latex did not show any sign of colloidal instability or sedimentation.			15
20				20
	EXAMPLE 2			
25	An aqueous phase (W) and a monomer phase (M) were emulsified:			25
	<i>Aqueous phase (W):</i>			
	Desalted water	85.0 parts by weight		
	Paraffin sulphonate	3.5 parts by weight		
30	Potassium peroxydisulphate	0.005 part by weight	30	
	<i>Monomer phase (M):</i>			
	Chloroprene (stabilised with 100 ppm of phenothiazine)	98.0 parts by weight		
35	Methacrylic acid (stabilised with 50 ppm of hydroquinone methyl ether)	2.0 parts by weight	35	
	<i>n</i> -dodecyl mercaptan	0.2 part by weight		
40	The emulsion was heated to 40°C with stirring under a nitrogen atmosphere. The reaction began following the addition of a small quantity of 2.5% aqueous formamidine sulphinic acid and the temperature rose to 48°C. The polymerisation temperature was kept between 45 and 50°C by cooling and regulating the dropwise addition rate of the activator solution. Polymerisation was over after 4.5 hours. The evaporation concentration amounted to 52.5%, pH: 4.5. No coagulate had formed. The conversion was approximately 99% after standing for 2 months, the latex did not show any signs of sedimentation or colloidal instability.			40
45				45
	EXAMPLE 3			
50	An aqueous phase (W) and a monomer phase (M) were emulsified:			50
	<i>Aqueous phase (W):</i>			
	Desalted water	85.0 parts by weight		
	Paraffin sulphonate	3.5 parts by weight		
55	Adduct of 1 mole of stearyl alcohol and 20 moles of ethylene oxide	1.5 parts by weight	55	
	Condensation product of naphthalene sulphonic acid and formaldehyde	0.4 part by weight		
60	Adduct of 1 mole of <i>i</i> -nonyl phenol and 10 moles of ethylene oxide	0.2 part by weight	60	
65				65

	Disodium hydrogen phosphate	0.25 part by weight	
	Sodium dihydrogen phosphate	0.25 part by weight	
	Potassium peroxydisulphate	0.02 part by weight	
5	<i>Monomer phase (M):</i>		5
	Chloroprene (stabilised with 100 ppm of phenothiazine)	96.0 parts by weight	
10	Methacrylic acid (stabilised with 50 ppm of hydroquinone methyl ether)	4.0 parts by weight	10
	<i>n</i> -dodecyl mercaptan	0.20 part by weight	
15	Polymerisation took place in the same way as described in Example 1. The reaction was over after 3.5 hours. The evaporation concentration of the latex amounted to 54.1 % by weight, pH: 6.5. No coagulate had formed during polymerisation. The conversion amounted to more than 99%. After standing for 2 months, the latex did not show any signs of sedimentation or colloidal instability.		
20	<i>Example 4</i>		20
	An aqueous phase (W) and a monomer phase (M) were emulsified:		
	<i>Aqueous phase (W):</i>		
	Desalted Water	85.0 parts by weight	
25	Paraffin sulphonate	3.0 parts by weight	25
	Adduct of 1 mole of stearyl alcohol and 20 moles of ethylene oxide	1.0 part by weight	
30	Adduct of 1 mole of <i>i</i> -nonyl phenol and 10 moles of ethylene oxide	0.3 part by weight	30
	Condensation product of naphthalene- β -sulphonic acid and formaldehyde	0.5 part by weight	
	Potassium peroxydisulphate	0.01 part by weight	
35	<i>Monomer phase (M):</i>		35
	Chloroprene (stabilised with 200 ppm of pheno- thiazine)	99.0 parts by weight	
40	Methacrylic acid (stabilised with 50 ppm of hydro- quinone methyl ether)	1.0 part by weight	40
	<i>n</i> -dodecyl mercaptan	0.30 part by weight	
45	Polymerisation was carried out in the same way as described in Example 1. It was not accompanied by any precipitation. The reaction was over after 2 hours by which time the evaporation concentration had reached 54.2% by weight, pH: 5.0. The conversion was approximately 99%. After standing for 2 months, the latex did not show any sign of sedimentation or colloidal instability.		
50	<i>Example 5</i>		50
	An aqueous phase (W) and a monomer phase (M) were emulsified:		
	<i>Aqueous phase (W):</i>		
	Desalted water	83.0 parts by weight	
55	Isododecyl benzene sulphonate	3.0 parts by weight	55
	Condensation product of naphtha- lene sulphonic acid and formaldehyde	0.5 part by weight	
60	Adduct of 1 mole of <i>i</i> -nonyl phenol and 10 moles of ethylene oxide	0.2 part by weight	60
	Potassium peroxydisulphate	0.001 part by weight	
	<i>Monomer phase (M):</i>		
65	Chloroprene (stabilised with 100 ppm of pheno- thiazine)	97.0 parts by weight	65

Acrylic acid
(stabilised with 150 ppm of hydro-
quinone methyl ether) 3.0 parts by weight
n-dodecyl mercaptan 0.15 part by weight

5 The emulsion was heated to 40°C with stirring under a nitrogen atmosphere. Polymerisa- 5
tion began following the addition of 2.5% formamidine sulphinic acid solution. After the
reaction surge, during which the temperature rose to 50°C, had abated, the activator solution
was added dropwise in such a way that the temperature fluctuated around 45°C. The reaction
10 was over after 3 hours. The evaporation concentration amounted to 55.3% by weight, pH: 10
3.6. No coagulate had formed during polymerisation. The conversion was approximately
99%. After standing for 2 months, the latex did not show any signs of sedimentation or
colloidal instability.

WHAT WE CLAIM IS:-

- 15 1. A process for the production of concentrated polychloroprene latices containing 15
reactive groups, which comprises copolymerising chloroprene with an olefinically unsatu-
rated carboxylic acid in the presence of from 75 to 95 parts by weight of water and from 3 to 6
parts by weight of at least one ionic emulsifier active in the acid and neutral pH-range, and
optionally from 0.5 to 6 parts by weight of at least one non-ionic emulsifier and from 0.2 to 2
20 parts by weight of one or more other surface active substances, based in each case on 100 20
parts by weight of the total monomer mixture, the polymerisation being carried out at a pH
value of ≤ 7 and at a temperature of from 30 to 70°C up to a monomer conversion of at least
90% by weight.
2. A process as claimed in Claim 1, wherein the carboxylic acid is a mono- or dicarboxylic 25
acid.
3. A process as claimed in Claim 2, wherein the carboxylic acid is a monocarboxylic acid. 25
4. A process as claimed in any of Claims 1 to 3, wherein the carboxylic acid constitutes
from 0.5 to 10 parts by weight per 100 parts by weight of the total monomer mixture.
5. A process as claimed in any of Claims 1 to 4, wherein the polymerisation is carried out
30 at a temperature of from 40 to 65°C. 30
6. A process as claimed in any of Claims 1 to 5, wherein the pH is from 3 to 6.5. 30
7. A process as claimed in any of Claims 1 to 6, wherein the polymerisation is carried out
up to a monomer conversion of from 97 to 99.8% by weight.
8. A process as claimed in Claim 1, substantially as herein described with reference to any
35 of the specific Examples. 35
9. Polychloroprene latices when prepared by a process as claimed in any of Claims 1 to 8. 35

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